Understanding and Strategies for Controlled Interfacial Phenomena in Lithium-Ion Batteries and Beyond

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June 13th, 2019

Project ID #: bat329

Overview

Timeline

- Start date: October 1, 2016
- End date: September 30, 2019
- Percent complete: 80%

Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials degradation during cycling
  - Lifetime of the cell

Budget

- Total funding: $1,333,335
  - DOE share: $1,200,000
  - Contractor share: $133,335
- Funding received
  - FY18: $416,346
  - FY19: $399,844

Partners

- Interactions/ collaborations
  - J. Seminario (TAMU Co-PI)
  - P. Mukherjee (Purdue U. Co-PI)
  - M. Vijayakumar (PNNL)
- Project lead: TAMU

Relevance

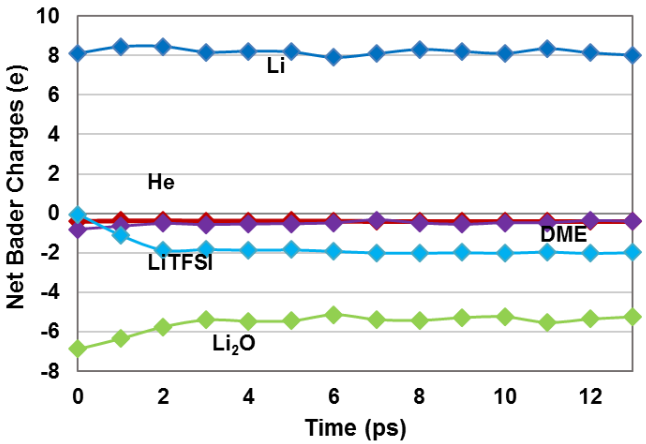
- **Objective:** Evaluate and characterize *interfacial phenomena* in lithiated Si and Li metal anodes and develop strategies leading to *controlled reactivity* at electrode/electrolyte interfaces using advanced modeling techniques based on first-principles.
- **FY 2019 goals**: Characterize **Li deposition** as a function of surface structure and deposition rates; identify **environment effects** (electrolytes, SEI, applied field) on Li deposition and initial nucleation.
- **Addressing targets and barriers**:
  - Understand and model life-limiting mechanisms taking into account microscopic phenomena.
- **Impact:**
  - Implementation of *stable* Si alloys and Li metal anodes depends on *structural evolution* during battery operation. **Understanding** SEI reactions, Li deposition and nucleation, and effects of applied potential **leads to rational** electrolyte and electrode architecture **design**.

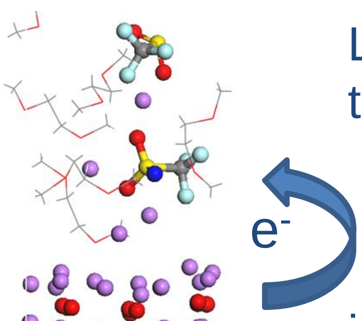
Approach

- **Methods to achieve goals**:
  - Interfacial problems (Li deposition and nucleation, SEI formation) addressed with *synergistic multiscale modeling* (ab initio, classical molecular dynamics, and mesoscopic level models).
  - All findings rigorously compared with experimental evidence. First-principles approach allows prediction and interpretation of observed and new phenomena.
  - Addresses technical barriers/targets: SEI nucleation near Li deposits as a function of electrolyte composition and applied potential characterizes *SEI evolution*. SEI reforming and dendrites formation elucidate *anode capacity loss* and *cell lifetime*.
  - Collaboration within TAMU and Purdue U. and with experimental groups (PNNL).

- **Progress towards FY19 milestones**: SEI chemistry and reactivity explained. Effect of applied potential on Li deposition identified. Dendrite nucleation and growth analyzed at nano and mesoscopic levels.

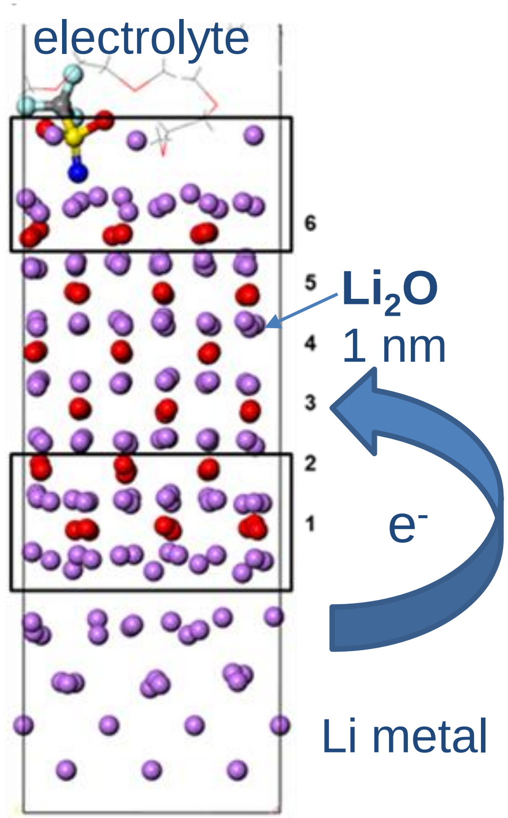
Technical Accomplishments:
Reactivity on Li surfaces





SO_2CF_3 = -0.05 |e|
NSO_2CF_3 = -1.81 |e|

Li_2O stores and transfers e$^-$. Charges accumulate at Li_2O/electrolyte interface; LiTFSI decomposes.



"Natural" SEI:

Even the cleanest Li metal surface has impurity-layers (Li_2O, Li_2CO_3, LiOH):

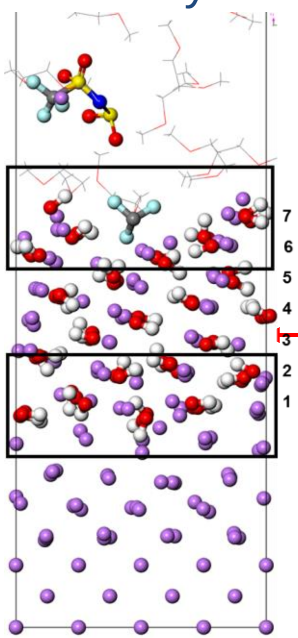
Does reactivity change on this modified surface?

Collaboration with XPS analysis (PNNL, Vijayakumar Murugesan) + AIMD simulations (TAMU)

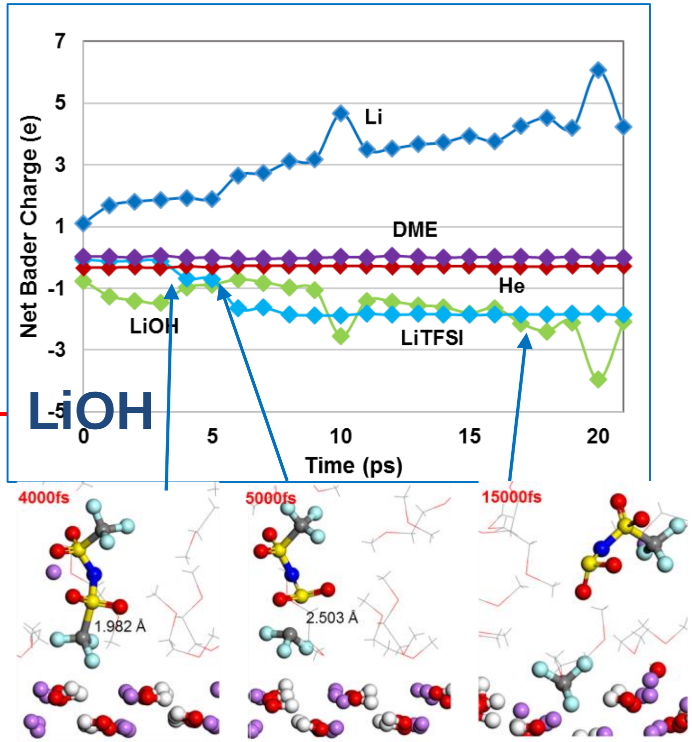
Li_2O able to store charge. Keeps ordered structure. Top Li metal layers oxidize; top oxide layers accumulate charge. Limited passivation.

Technical Accomplishments:
Reactivity on Li surfaces

electrolyte



Li metal



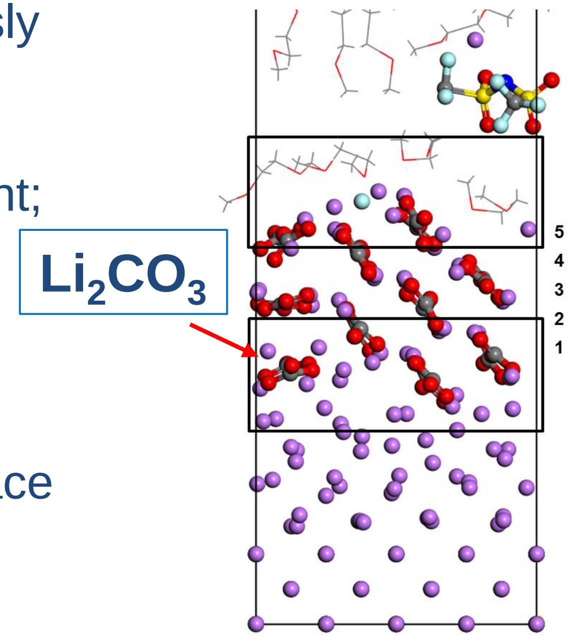
LiTFSI = -0.67 |e|

LiTFSI = -0.71 |e|

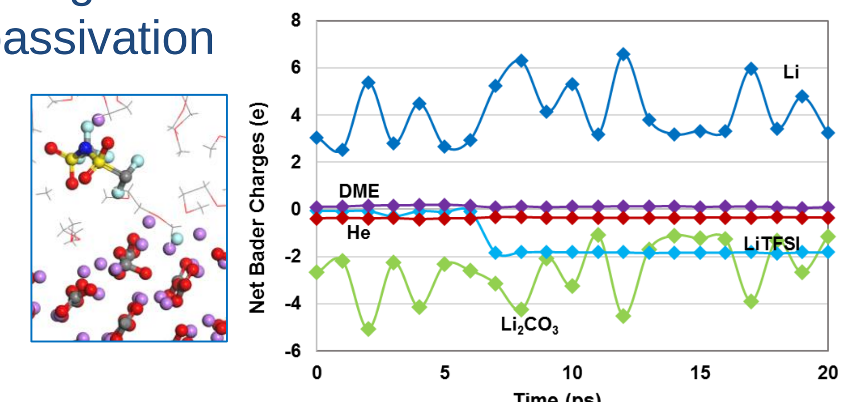
Li($SO_2NSO_2CF_3$) = -0.96 |e|
CF_3 = -0.89 |e|

Li_2CO_3 stores but continuously exchanges charge w/ Li. Dipoles reorient; structure becomes amorphous. Bottom $CO_3^=$ groups (interface w/ Li) accumulate charge. Limited passivation

electrolyte



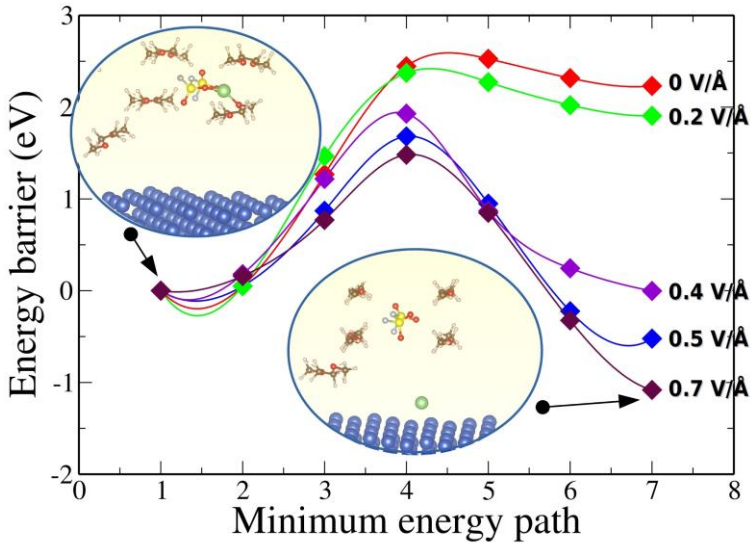
Li metal



Li($CF_2SO_2NSO_2CF_3$) = -1 |e|; F = -1 |e|

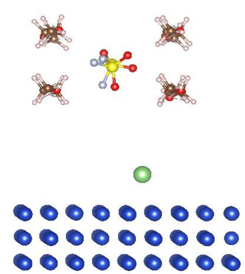
LiOH stores charge (less than Li_2O). Dipoles reorient; structure becomes amorphous. Bottom OH groups (interface w/ Li) accumulate charge. Limited passivation.

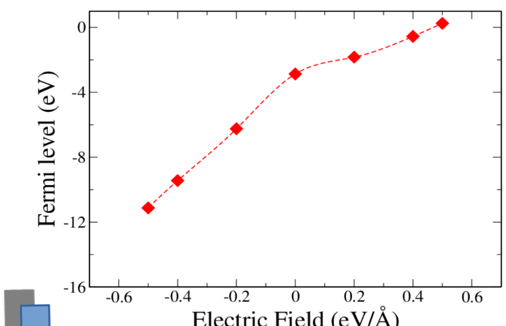
Technical Accomplishments:
Applied potential effect on Li electrodeposition



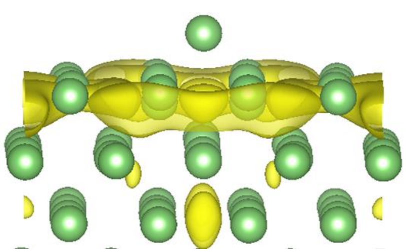
Even though Cu is a noble metal, electric field (EF) polarizes the surface, Fermi level "shifts" to the right, Li ion orbitals become occupied.

Longo, Camacho, Balbuena, *J. Mater. Chem. A*, 2019

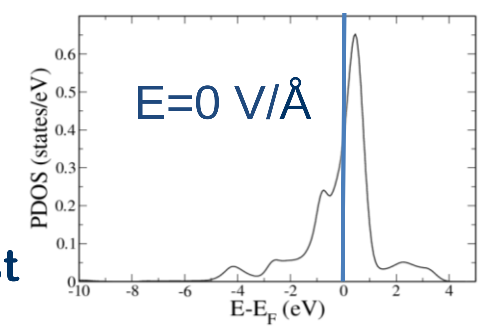


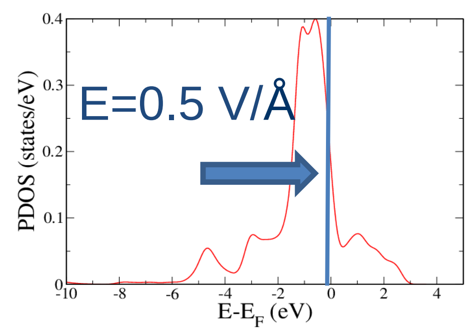


In absence of EF, Li^{+} deposition is endothermic. As EF ⇧ it becomes exothermic and energy barrier decreases. Li surfaces favor reduction at the cost of stability.



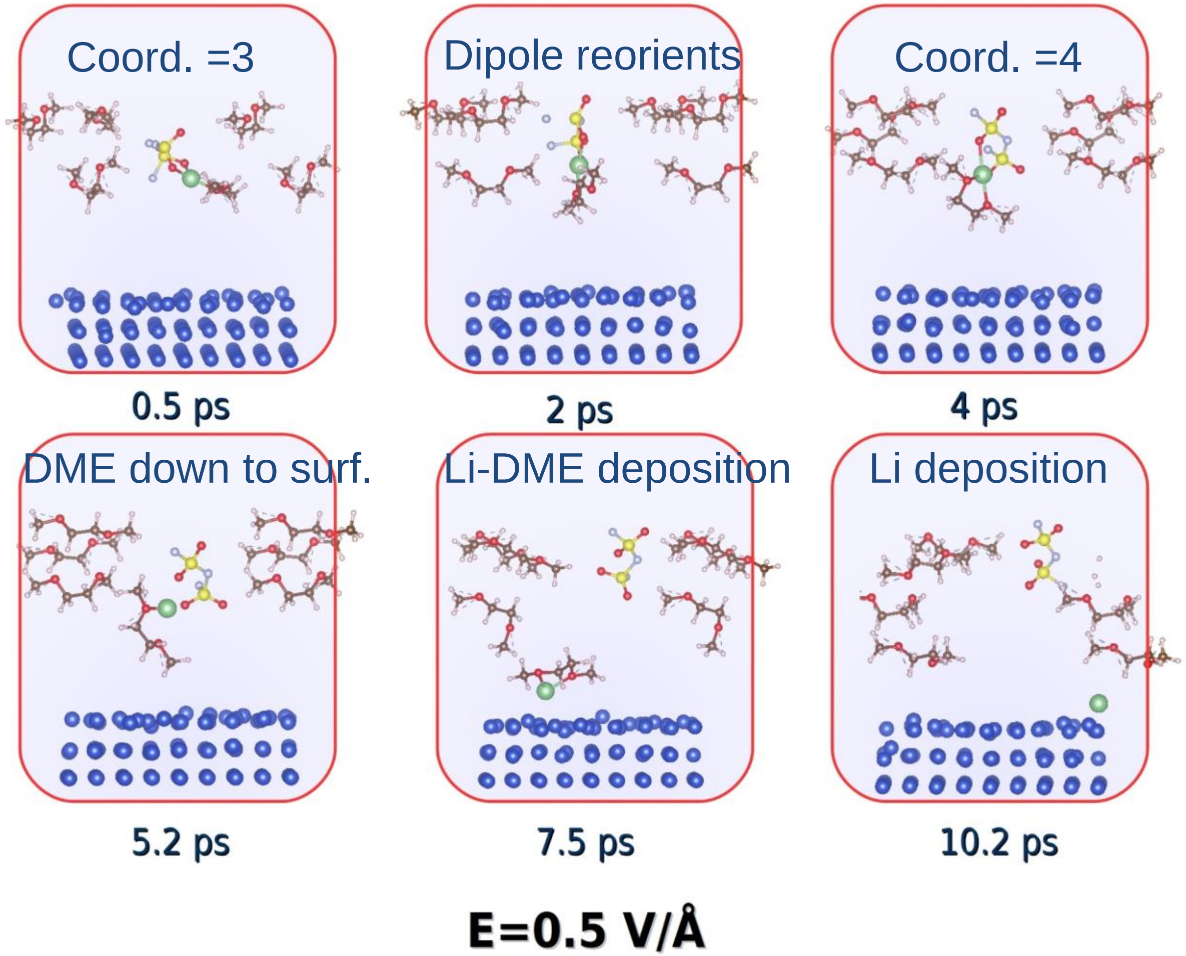
Li(001) surface polarization orbitals created at E=0.5 V/Å. These orbitals do not exist for Cu(001).





Technical Accomplishments:
Electrolyte effects on Li electrodeposition

1M LiFSI in DME; EF = 0.5 V/Å

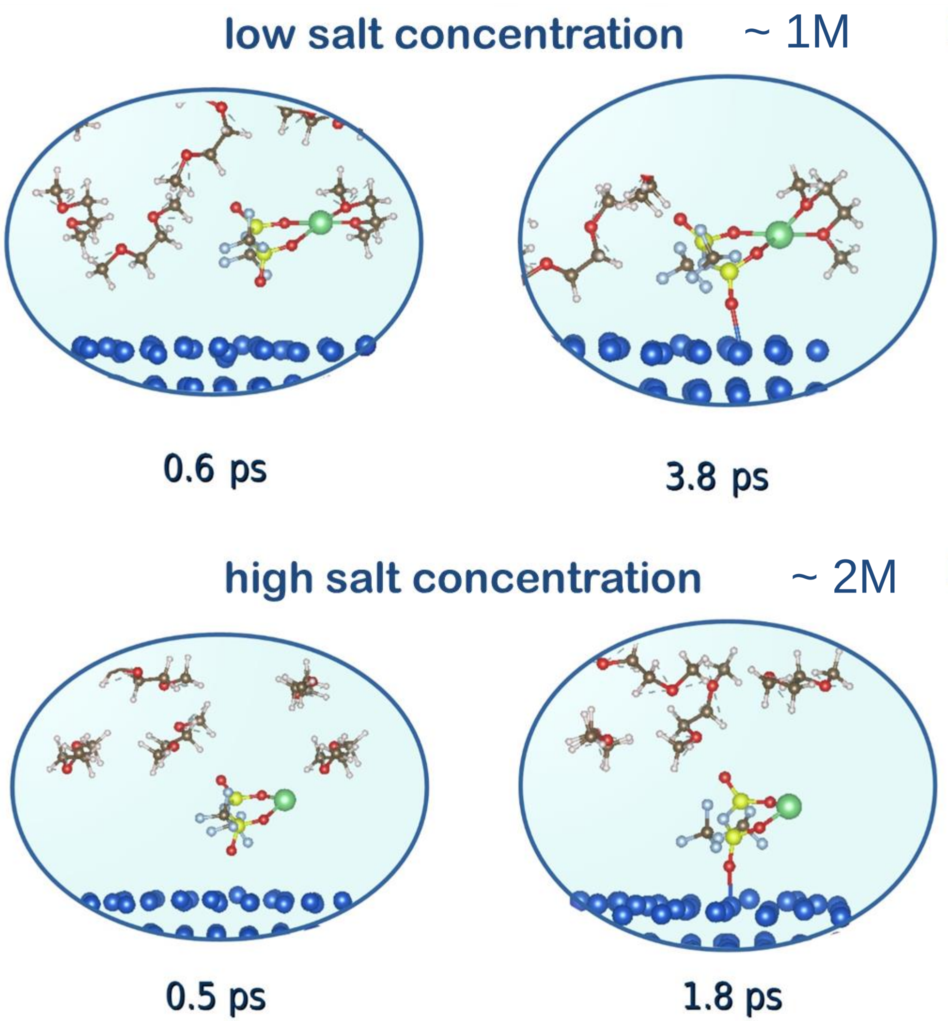


Effective screening medium- AIMD simulations of the Li deposition process

Clear solvent effect on cation deposition

Longo, Camacho, Balbuena, *J. Mater. Chem. A*, 2019

Technical Accomplishments:
Electrolyte effects on Li electrodeposition



DME/LITFSI Simulation at constant potential: 0.4 V (intermediate bias)

At low salt concentration, solvent deposits with anion and cation (SEI from all components)

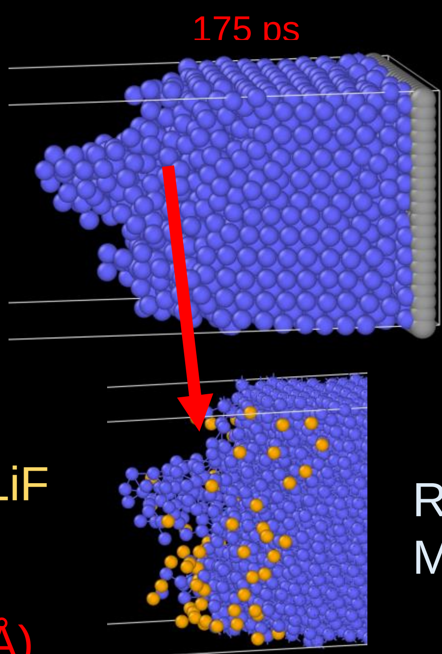
At higher salt concentration, ion pair deposits (SEI from anion)

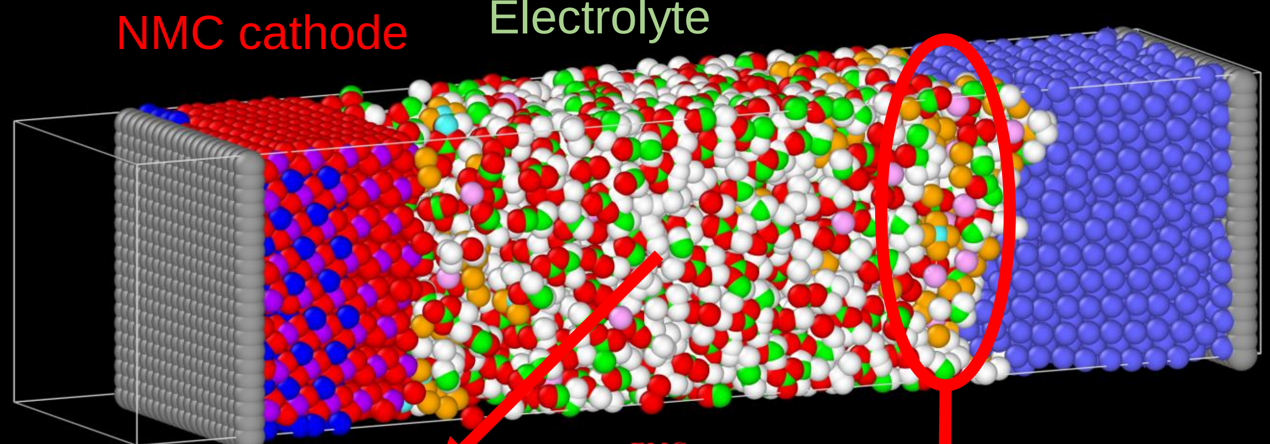
Longo, Camacho, Balbuena, *J. Mater. Chem. A*, 2019

Technical Accomplishments: Initial nucleation stages

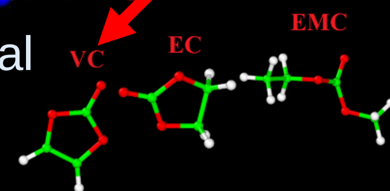
LiF forming near nucleation sites

Selis and Seminario, to be submitted

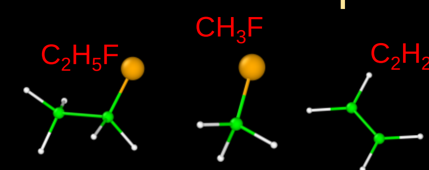


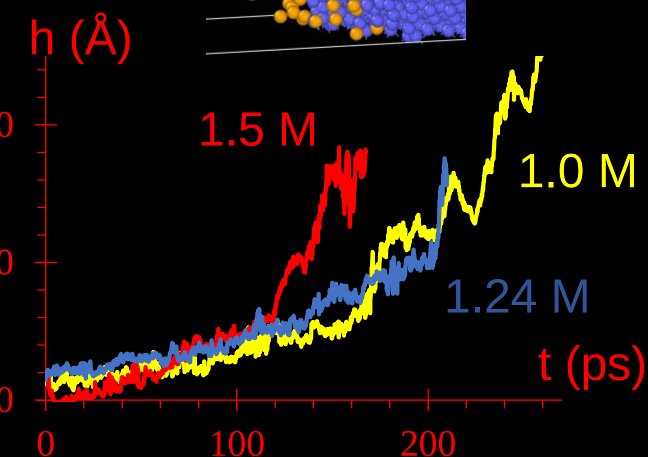


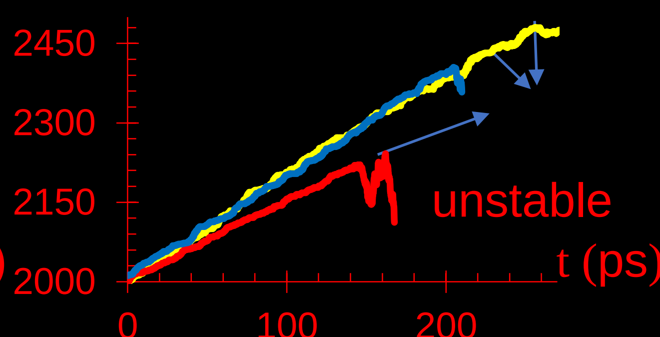
Results from classical MD simulations

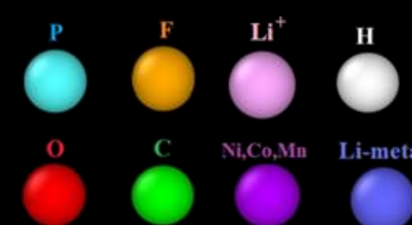


additional SEI products





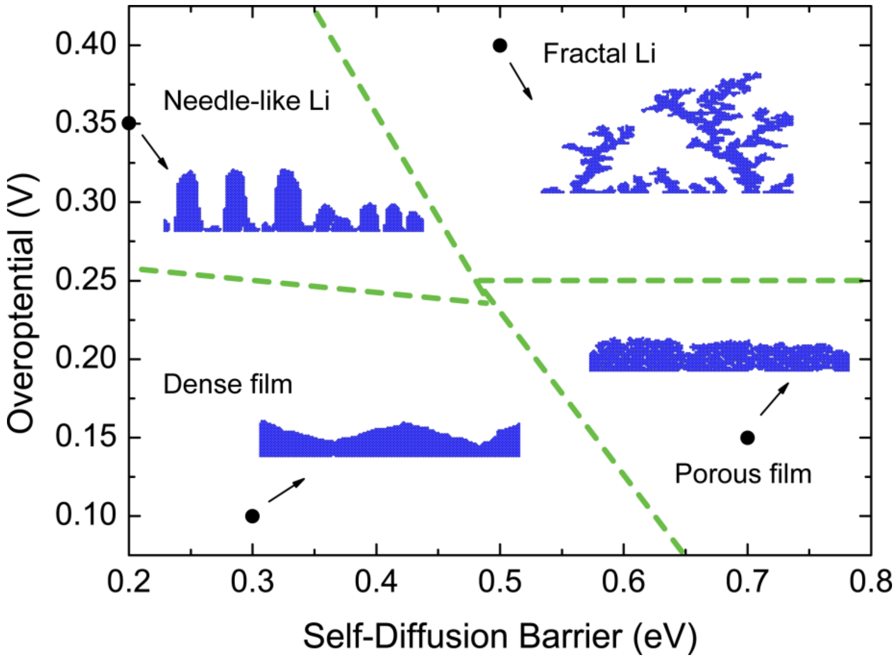


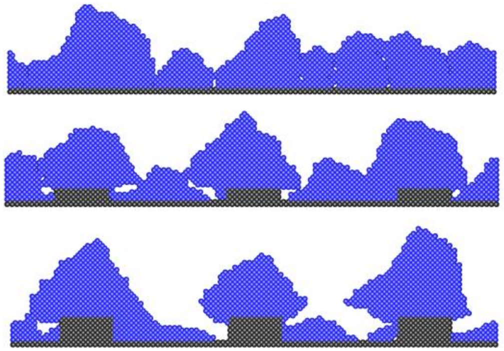


height (h) of nucleating structures depends on salt concentration

# of anode atoms increase due to nucleation; instabilities depend on salt concentration

Technical Accomplishments:
Electrodeposition Morphology for Li Metal Anodes

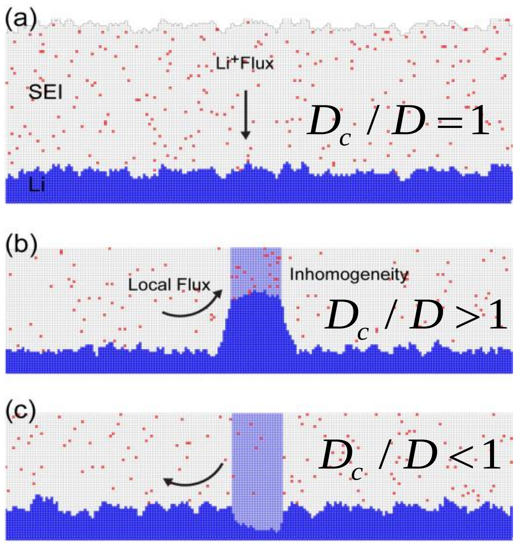




substrate roughness effect

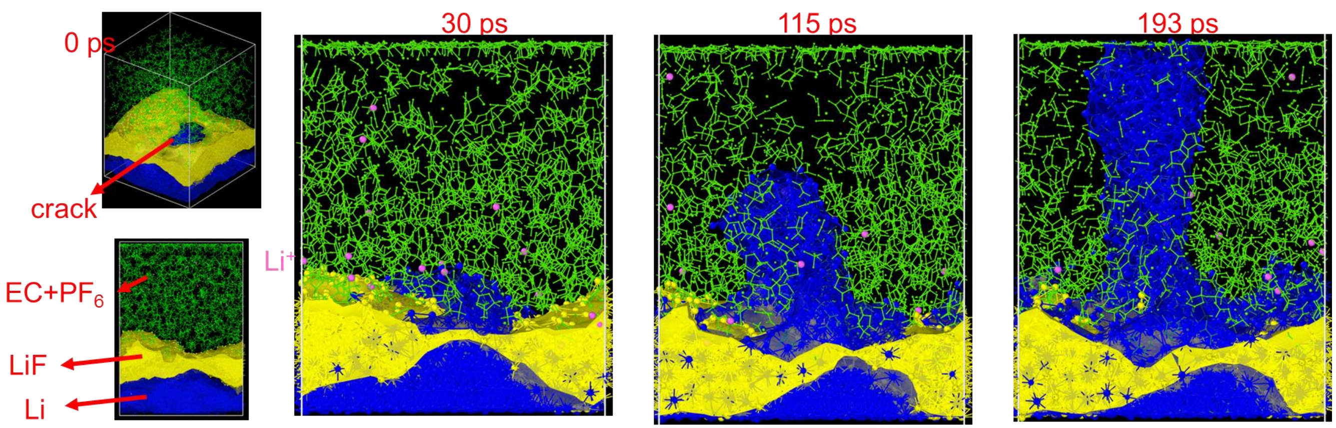
Hao, Verma and Mukherjee, *ACS Appl. Mater. & Interfaces*, **10**, 26320 (2018)

non-uniform Li flux through SEI leads to interfacial stress distribution



Hao, Verma and Mukherjee, *J. Mater. Chem. A*, **6**, 19664 (2018)

From classical MD, growth evolution through SEI cracks



Selis and Seminario, to be submitted

ratio D_c/D reflects SEI inhomogeneity; D_c is the Li diffusion in the center of the SEI

Collaboration and Coordination with Other Institutions

- Texas A&M University (prime) and Purdue U. (sub-awardee): Prof. Jorge Seminario (Co-PI, TAMU), classical MD simulations, and Prof. Partha Mukherjee (Co-PI, Purdue), mesoscopic modeling, have contributed large part of the reported work.

- PNNL: Experimental (M. Vijayakumar) and theoretical characterization of electrolyte reduction over Li metal surfaces (TAMU) covered by selected SEI components

Proposed Future Research

- **FY19:**
  - identify relationships between electrolyte chemical/electrochemical properties, salt concentration, and interfacial structure and Li metal electronic distribution → deposition/nucleation
  - develop alternative charging strategies for Li metal anodes

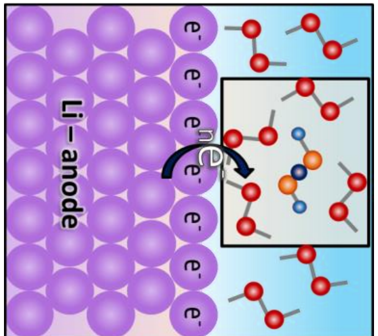
Any proposed future work is subject to change based on funding levels

Summary Slide

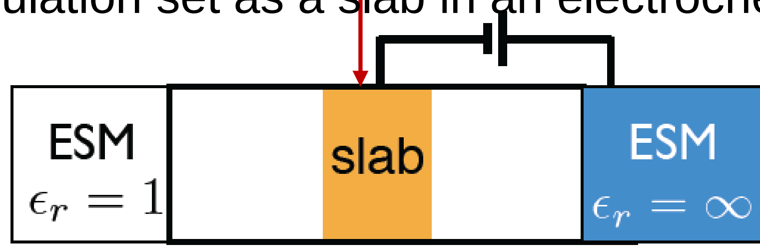
- **Relevance:** **Elucidation of SEI formation and dendrite formation on Li metal are crucial for *controlling irreversible capacity loss* and *improving lifetimes*.**
- **Approach:** **Characterization of issues that impede extended lifetimes on Li metal anodes via *multiscale modeling*: from electronic structure and dynamics, through atomistic classical molecular dynamics, and mesoscopic modeling.**
- **Technical Accomplishments:** **passivation role of natural SEI layer on Li metal; effects of applied potential on Li deposition and SEI formation; multiscale characterization of deposition morphology, and dendrite nucleation and growth.**
- **Collaborations:** **Synergistic multiscale modeling approach (TAMU/Purdue); passivation role of SEI (with PNNL).**
- **Future Work:** **Identify link between electrolyte properties, structure, and salt concentration with Li nucleation. Study alternative charging strategies.**

Technical Back-Up Slides

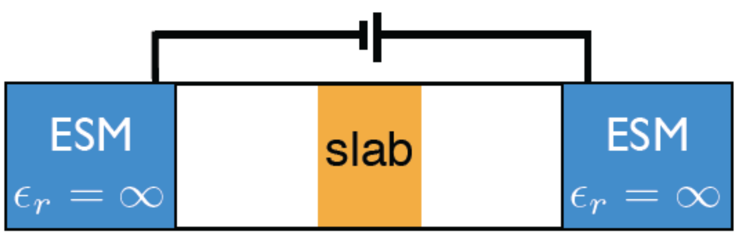
Electrode/electrolyte interface



Simulation set as a slab in an electrochemical cell



Simulation set as a slab in a capacitor



Effects included in AIMD (shown in slides 5 and 6)

- Ionic distribution
- Screening effect of electrolyte
- Interaction metal/electrolyte
- Electronic structure

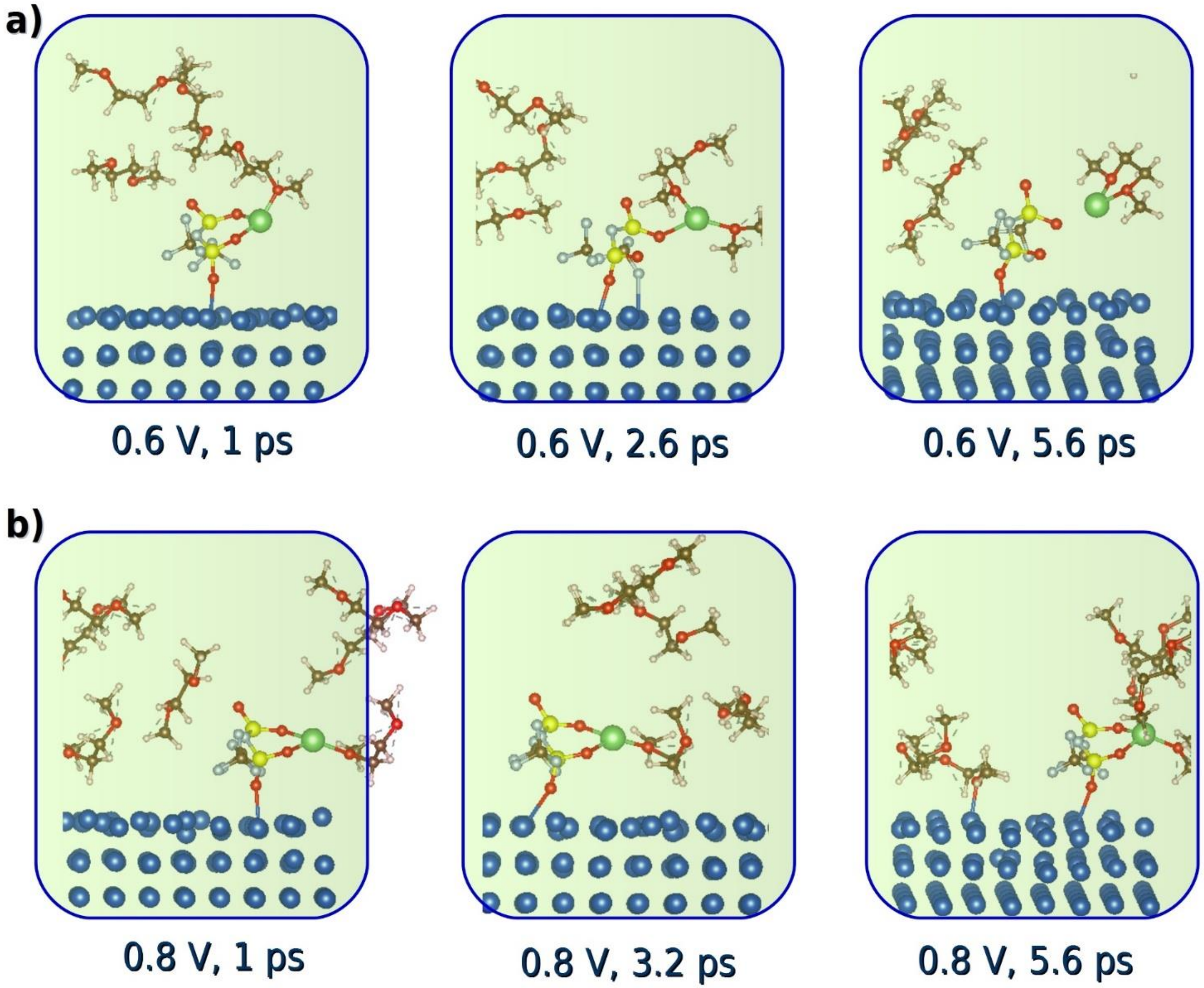
In addition, first principles molecular dynamics under a bias potential: **AIMD + ESM** (effective screening method) shown in slides 7, 8, 9 include:

- Bias potential
- Electrical double layer

ESM method from Otani and Sugino, PRB, 73, 115407 (2006)

Longo, Camacho, Balbuena, J. Mater. Chem. A, 2019

What happens at very high potentials

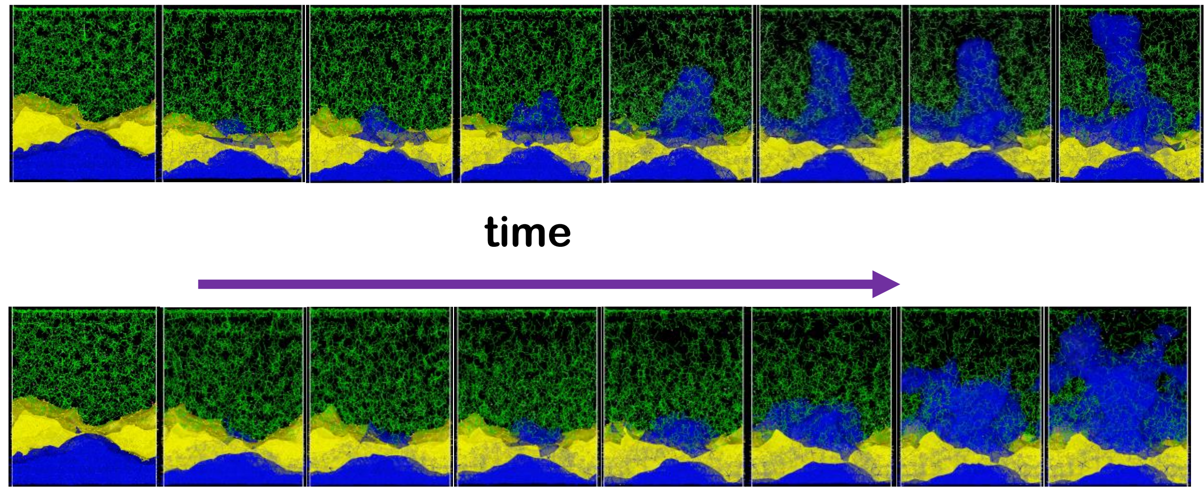


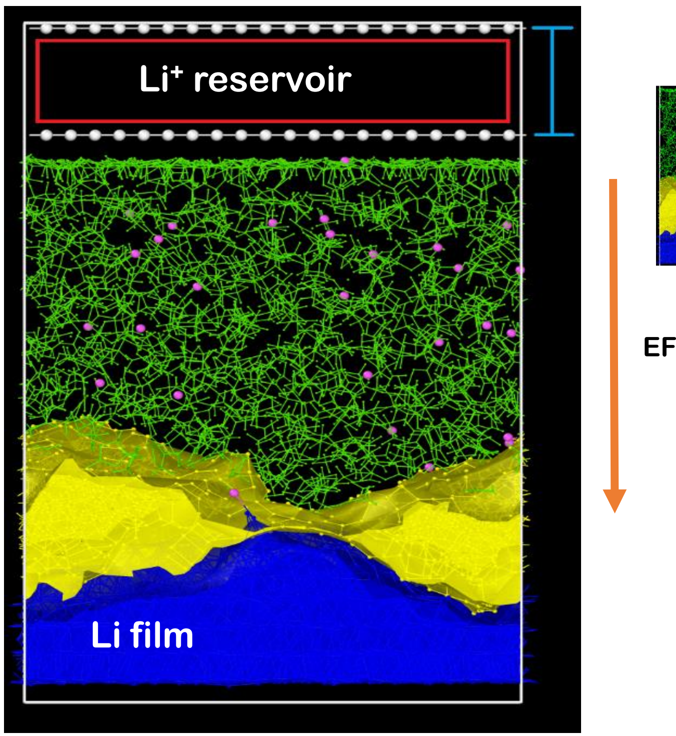
DME/LITFSI
Simulation at constant potential
high bias;
high salt concentration:
0.6 V
anion deposition

very fast reactions

0.8 V
low salt concentration
deposition of solvent + complex

Molecular dynamics analysis of dendrite growth on a SEI-covered Li film

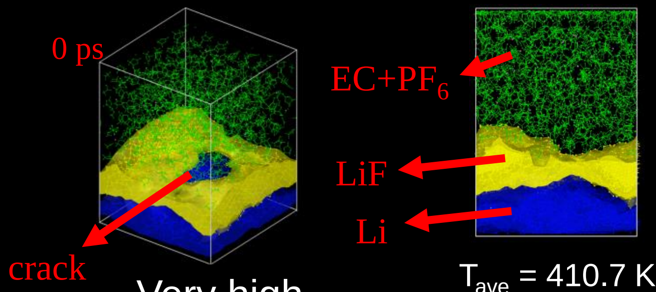




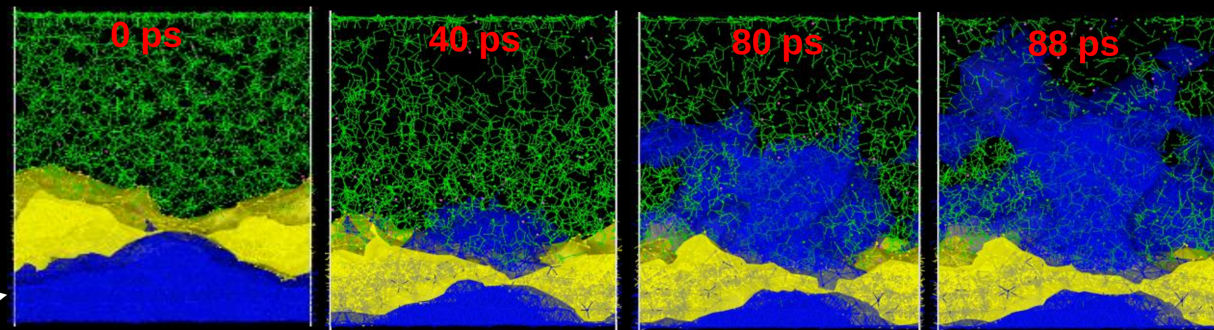
- Li ions diffuse toward the Li electrode under an EF
- Model SEI (LiF) is an inhomogeneous film with cracks
- Li ions can land anywhere on the surface, and diffuse through the SEI, but dendritic growth is detected only through cracks
- Mode of growth is followed for various current rate values and pulse charge conditions
- SEI reactions keep occurring during Li electrodeposition

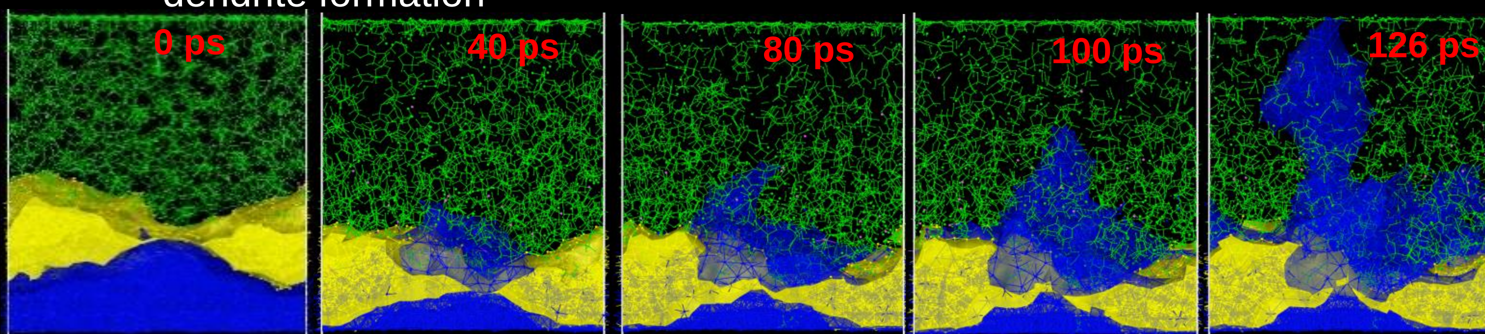
Selis and Seminario, to be submitted

Effect of temperature on dendrite growth from classical MD simulations: Li ions move through the SEI (yellow) and also deposit on the crack. When they get reduced underneath the crack the nucleated phase exerts pressure and grows further.



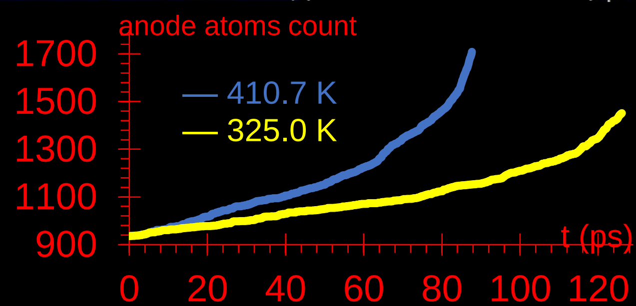
Very high temperatures hinder dendrite formation

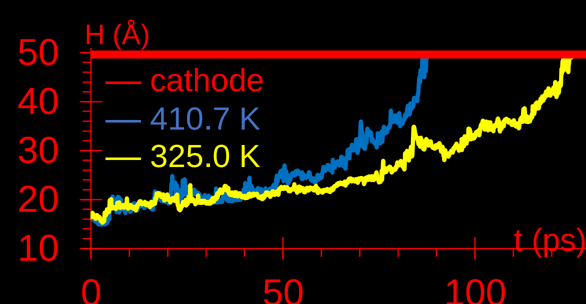


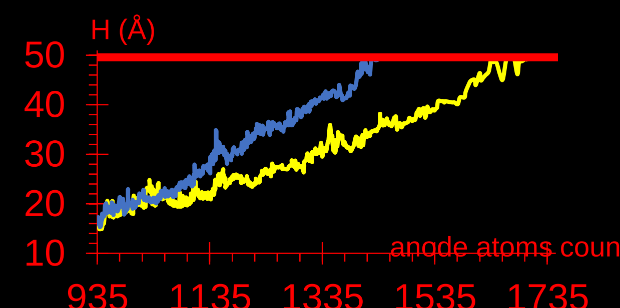


Dendrite shape depends of temperature

T_{ave} = 325.0 K



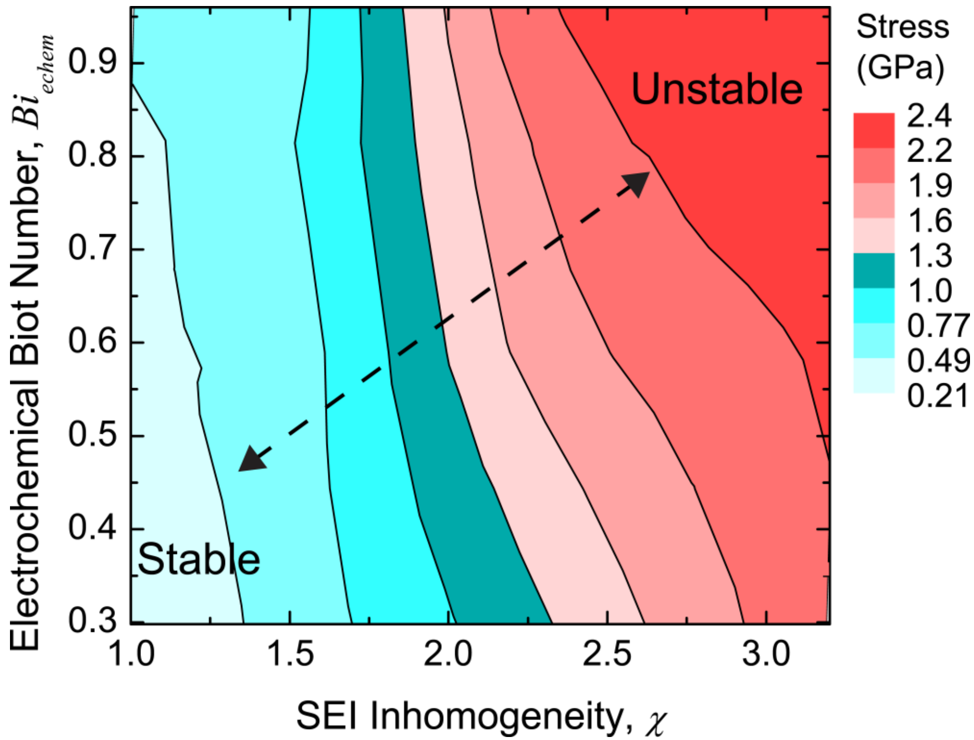




At higher T, deposition is faster, but shape is less dendritic (more amorphous)

Li Deposition under Inhomogeneous SEI

- For the two parameters: 1. SEI inhomogeneity, χ: D_c is the diffusivity of the center region, and D is the diffusivity of other region. 2. Electrochemical Biot number, Bi_{echem}: i is the current density, h the SEI thickness, c_0 Li-ion concentration in SEI. SEI inhomogeneity primarily determines the stress in SEI. If SEI has a yield stress of 1 GPa, SEI with a inhomogeneity larger than 2 will fracture. (SEI, mechanical parameters: Young's modulus 10 GPa, Poisson's ratio 0.3)



$$Bi_{echem} = \frac{ih}{c_0 D}, \ \chi = \frac{D_c}{D}$$

Uneven Li plating is obtained due to nonuniform Li flux through the SEI layer leading to interfacial stress distribution and affecting stability.